

Identity for the second functional derivative of the density functional Hartree plus exchange-correlation functional.

Daniel P. Joubert*

Centre for Theoretical Physics, University of the Witwatersrand, PO Wits 2050, Johannesburg, South Africa

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It is shown that the second functional derivative of the density functional Hartree plus exchange-correlation functional satisfies

$$\int d^3 r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta E_{hxc}^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r}') \delta \rho_N(\mathbf{r})} = \text{constant}.$$

$\rho_N(\mathbf{r})$ and $\rho_{N-1}^\gamma(\mathbf{r})$ are N -electron and $(N-1)$ -electron densities determined from the same adiabatically scaled Hamiltonian of the interacting electron system with γ the scaling parameter of the electron-electron interaction strength.

I. INTRODUCTION

The Kohn-Sham (KS) formulation [2] of Density Functional Theory (DFT) [3] has become the de facto tool for the calculation of electronic structure of molecules and solids. In all practical applications of DFT, however, approximations to the exact functionals have to be made [4–8]. Properties of density functionals that give an indication of the internal structure of the functionals can give insight and help with the development of accurate approximations to the exact functionals [9].

There is little known about the properties of the second functional derivatives of important functionals. From structural stability arguments [10–12], for example, the second derivative of the density functional $F^\gamma[\rho]$, the sum of the kinetic and interaction energy functionals, is positive definite. Similarly for the non-interacting Kohn-Sham system, the second derivative of the non-interacting kinetic energy functional is positive definite. In this paper it is shown that the integral of the product of the charge density difference of the N and $(N-1)$ electron densities of the same Hamiltonian and the second functional derivative of the Hartree plus exchange-correlation functional of the N -electron density is equal to a constant:

$$\int d^3 r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta E_{hxc}^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r}') \delta \rho_N(\mathbf{r})} = \text{constant}. \quad (1)$$

Here ρ_N and ρ_{N-1}^γ are the ground state charge densities of an interacting N and $(N-1)$ electron system of the same Hamiltonian with multiplicative external potential $v_{\text{ext}}^\gamma([\rho_N])$. The potential $v_{\text{ext}}^\gamma([\rho_N])$ is constructed to keep the charge density of the N electron system independent of the coupling strength parameter γ [13–16] that scales the electron-electron interaction strength. At $\gamma = 1$ full strength Coulomb interaction between electrons is included and the external potential $v_{\text{ext}}^\gamma([\rho_N])$ is the external potential of the fully interacting system, while $\gamma = 0$ corresponds to the non-interacting Kohn-Sham potential.

Equation (1) gives new insight into the internal structure of density functionals and can also be used to test approximate density functionals. The simplest test can be performed at full coupling strength, $\gamma = 1$. Two self-consistent calculations are required to determine ρ_N and ρ_{N-1}^1 and then (1) can be evaluated. Ideally an approximate exchange-correlation functional will satisfy this expression.

II. PROOF

In the adiabatic connection approach [13–16] of the constrained minimization formulation of density functional theory [2, 3, 10, 17] the Hamiltonian \hat{H}^γ for a system of N electrons is given by

$$\hat{H}^\gamma = \hat{T} + \gamma \hat{V}_{ee} + \hat{v}_{N,\text{ext}}^\gamma[\rho_N]. \quad (2)$$

*Electronic address: daniel.joubert2@wits.ac.za

Atomic units, $\hbar = e = m = 1$ are used throughout. \hat{T} is the kinetic energy operator,

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \quad (3)$$

and $\gamma \hat{V}_{ee}$ is a scaled electron-electron interaction,

$$\gamma \hat{V}_{ee} = \gamma \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (4)$$

The external potential

$$\hat{v}_{\text{ext}}^\gamma [\rho_N] = \sum_{i=1}^N v_{\text{ext}}^\gamma ([\rho_N]; \mathbf{r}_i), \quad (5)$$

is constructed to keep the charge density fixed at $\rho_N(\mathbf{r})$, the ground state charge density of the fully interacting system ($\gamma = 1$), for all values of the coupling constant γ . The external potential has the form [17, 18]

$$\begin{aligned} v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}) &= (1 - \gamma) v_{hx}([\rho_N]; \mathbf{r}) \\ &+ v_c^1([\rho_N]; \mathbf{r}) - v_c^\gamma([\rho_N]; \mathbf{r}) + v_{\text{ext}}^1([\rho_N]; \mathbf{r}), \end{aligned} \quad (6)$$

where $v_{\text{ext}}^1([\rho_N]; \mathbf{r}) = v_{\text{ext}}(\mathbf{r})$ is the external potential at full coupling strength, $\gamma = 1$, and $v_{\text{ext}}^0([\rho_N]; \mathbf{r})$ is the non-interacting Kohn-Sham potential. The exchange plus Hartree potential [11, 12] $v_{hx}([\rho_N]; \mathbf{r})$ is independent of γ , while the correlation potential $v_c^\gamma([\rho_N]; \mathbf{r})$ depends in the scaling parameter γ . The chemical potential

$$\mu = E_N^\gamma(v_{\text{ext}}^\gamma[\rho]) - E_{N-1}^\gamma(v_{\text{ext}}^\gamma[\rho]) \quad (7)$$

depends on the asymptotic decay of the charge density [11, 12, 19, 20] and hence is independent of the coupling constant γ [21, 22]. In Eq. (7) E_{N-1}^γ is the groundstate energy of the $(N-1)$ -electron system with the same single-particle external potential $v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r})$ as the N -electron system:

$$\begin{aligned} \hat{H}_M^\gamma |\Psi_{\rho_M^\gamma}^\gamma\rangle &= E_M^\gamma |\Psi_{\rho_M^\gamma}^\gamma\rangle \\ \hat{H}_M^\gamma &= \hat{T} + \gamma \hat{V}_{ee} + \hat{v}_{M,\text{ext}}^\gamma[\rho_N] \\ \hat{v}_{M,\text{ext}}^\gamma[\rho_N] &= \sum_{i=1}^M v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}_i) \end{aligned} \quad (8)$$

The energy functional $F^\gamma[\rho]$ is defined as [10–12]

$$\begin{aligned} F^\gamma[\rho] &= \langle \Psi_\rho^\gamma | \hat{T} + \gamma \hat{V}_{ee} | \Psi_\rho^\gamma \rangle \\ &= \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \gamma \hat{V}_{ee} | \Psi \rangle, \end{aligned} \quad (9)$$

where according to the Levy constrained minimization formulation[10], the wavefunction $|\Psi_\rho^\gamma\rangle$ yields the density ρ and minimizes $\langle \Psi | \hat{T} + \gamma \hat{V}_{ee} | \Psi \rangle$. For v -representable densities [10–12], the densities are derived from the groundstate eigenfunctions of the Hamiltonian in (8). Note that by construction of $v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r})$, Eq. (6) $\rho_N = \rho_N^1$ is independent of γ , but the groundstate density of the $(N-1)$ -electron system ρ_{N-1}^γ is expected to be a function of γ . $F^\gamma[\rho]$ is usually decomposed as [11, 12]

$$F^\gamma[\rho] = T^0[\rho] + \gamma E_{hx}[\rho] + E_c^\gamma[\rho]. \quad (10)$$

The correlation energy $E_c^\gamma[\rho]$ is defined as [17]

$$\begin{aligned} E_c^\gamma[\rho] &= \langle \Psi_\rho^\gamma | \hat{T} + \gamma \hat{V}_{ee} | \Psi_\rho^\gamma \rangle \\ &- \langle \Psi_\rho^0 | \hat{T} + \gamma \hat{V}_{ee} | \Psi_\rho^0 \rangle, \end{aligned} \quad (11)$$

where $|\Psi_\rho^0\rangle$ is the Kohn-Sham independent particle groundstate wavefunction that yields the same density as the interacting system at coupling strength γ . $E_{hx}[\rho]$ is the sum of the Hartree and exchange energy

$$E_{hx}[\rho] = \langle \Psi_\rho^0 | \hat{V}_{ee} | \Psi_\rho^0 \rangle \quad (12)$$

and the kinetic energy functional $T^0[\rho]$ is given by

$$T^0[\rho] = \langle \Psi_\rho^0 | \hat{T} | \Psi_\rho^0 \rangle. \quad (13)$$

The full kinetic energy

$$\begin{aligned} T^\gamma[\rho] &= \langle \Psi_\rho^\gamma | \hat{T} | \Psi_\rho^\gamma \rangle \\ &= T^0[\rho] + T_c^\gamma[\rho], \end{aligned} \quad (14)$$

with the correlation part of the kinetic energy defined as

$$T_c^\gamma[\rho] = \langle \Psi_\rho^\gamma | \hat{T} | \Psi_\rho^\gamma \rangle - \langle \Psi_\rho^0 | \hat{T} | \Psi_\rho^0 \rangle. \quad (15)$$

Assuming that $F^\gamma[\rho]$ is defined for non-integer electrons [11, 12, 23], at the solution point

$$\frac{\delta F^\gamma[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{ext}}^\gamma([\rho]; \mathbf{r}) = \mu \quad (16)$$

where μ is the chemical potential. Note that by definition of $F^\gamma[\rho]$

$$\begin{aligned} E_N^\gamma(v_{\text{ext}}^\gamma[\rho_N]) &= F^\gamma[\rho_N] + \int d^3r \rho_N(\mathbf{r}) v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}) \\ E_{N-1}^\gamma(v_{\text{ext}}^\gamma[\rho_N]) &= F^\gamma[\rho_{N-1}^\gamma] + \int d^3r \rho_{N-1}^\gamma(\mathbf{r}) v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}). \end{aligned} \quad (17)$$

From (7) and (17),

$$F^\gamma[\rho_N] - F^\gamma[\rho_{N-1}^\gamma] = \mu - \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}). \quad (18)$$

Since

$$\int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) = 1, \quad (19)$$

it follows from (16), (18) and (19) that

$$F^\gamma[\rho_N] - F^\gamma[\rho_{N-1}^\gamma] = \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \frac{\delta F^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})}. \quad (20)$$

In a recent paper [24] the author showed that

$$\begin{aligned} &V_{ee}^\gamma[\rho_N] - V_{ee}^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r \frac{\delta V_{ee}^\gamma[\rho_N]}{\delta \rho_N^\gamma(\mathbf{r})} (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})). \end{aligned} \quad (21)$$

The proof of this equation is based on the virial theorem [17] of the interacting system.

The charge density ρ_N is independent of γ by construction, therefore from (10) and (12)

$$\frac{\partial}{\partial \gamma} F^\gamma[\rho_N] = E_{hx}[\rho_N] + \frac{\partial}{\partial \gamma} E_c^\gamma[\rho_N]. \quad (22)$$

The $(N - 1)$ -electron density ρ_{N-1}^γ is a function of γ , hence it follows from (10) and (12) that

$$\begin{aligned} \frac{\partial}{\partial \gamma} F^\gamma[\rho_{N-1}^\gamma] &= \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} \frac{\delta T^0[\rho_{N-1}^\gamma]}{\delta \rho_{N-1}^\gamma(\mathbf{r})} + E_{hx}[\rho_{N-1}^\gamma] \\ &+ \gamma \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} v_{hx}([\rho_{N-1}^\gamma]; \mathbf{r}) + \frac{\partial}{\partial \gamma} E_c^\gamma[\rho_{N-1}^\gamma], \end{aligned} \quad (23)$$

where $v_{hx}([\rho]; \mathbf{r}) = \frac{\delta E_{hx}[\rho]}{\delta \rho(\mathbf{r})}$. It follows from the definition of $E_c^\gamma[\rho_N]$, Eq. (11) that [17]

$$\frac{\partial}{\partial \gamma} E_c^\gamma[\rho_N] = \frac{1}{\gamma} (E_c^\gamma[\rho_N] - T_c^\gamma[\rho_N]). \quad (24)$$

The derivative $\frac{\partial}{\partial \gamma} E_c^\gamma[\rho_{N-1}^\gamma]$ is less simple since ρ_{N-1}^γ is a function of γ . From (11) it is clear that $E_c^\gamma[\rho_{N-1}^\gamma]$ depends on γ as the scaling parameter of the Coulomb interaction strength and via the dependence of the wavefunction $|\Psi_{\rho_{N-1}^\gamma}^\gamma\rangle$ on γ . It can be shown that [25]

$$\begin{aligned} &\frac{\partial}{\partial \gamma} E_c^\gamma[\rho_{N-1}^\gamma] \\ &= \frac{E_c^\gamma[\rho_{N-1}^\gamma] - T_c^\gamma[\rho_{N-1}^\gamma]}{\gamma} \\ &+ \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} (v_c^\gamma([\rho_N]; \mathbf{r}) + \gamma v_{hx}([\rho_N]; \mathbf{r}) - \gamma v_{hx}([\rho_{N-1}^\gamma]; \mathbf{r})) \end{aligned} \quad (25)$$

From (22), (23), (10), (24) and (25) it follows that

$$\begin{aligned} &E_{hxc}^\gamma[\rho_N] - T_c^\gamma[\rho_N] - (E_{hxc}^\gamma[\rho_{N-1}^\gamma] - T_c^\gamma[\rho_{N-1}^\gamma]) \\ &= \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \frac{\delta}{\delta \rho_N(\mathbf{r})} (E_{hxc}^\gamma[\rho_N] - T_c^\gamma[\rho_N]) \\ &+ \gamma \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} \left(\frac{\delta T^0[\rho_{N-1}^\gamma]}{\delta \rho_{N-1}^\gamma(\mathbf{r})} - \frac{\delta T^0[\rho_N]}{\delta \rho_N(\mathbf{r})} \right). \end{aligned} \quad (26)$$

Here $E_{hxc}^\gamma[\rho_N] = \gamma E_{hx}[\rho] + E_c^\gamma[\rho]$. From (9) and (10)

$$\gamma V_{ee}^\gamma[\rho] = E_{hxc}^\gamma[\rho_N] - T_c^\gamma[\rho], \quad (27)$$

and therefore from (26) and (21)

$$\int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} \left(\frac{\delta T^0[\rho_N]}{\delta \rho_N(\mathbf{r})} - \frac{\delta T^0[\rho_{N-1}^\gamma]}{\delta \rho_{N-1}^\gamma(\mathbf{r})} \right) = 0. \quad (28)$$

By construction, from (16) and (10)

$$\begin{aligned} &\frac{\delta T^0[\rho_N]}{\delta \rho_N(\mathbf{r})} + v_{hxc}^\gamma([\rho_N]; \mathbf{r}) + v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}) = \mu_N^\gamma \\ &\frac{\delta T^0[\rho_{N-1}^\gamma]}{\delta \rho_{N-1}^\gamma(\mathbf{r})} + v_{hxc}^\gamma([\rho_{N-1}^\gamma]; \mathbf{r}) + v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}) = \mu_{N-1}^\gamma \end{aligned} \quad (29)$$

where $v_{hxc}^\gamma([\rho]; \mathbf{r}) = \frac{\delta E_{hxc}^\gamma[\rho]}{\delta \rho(\mathbf{r})}$ and hence

$$\begin{aligned} &\frac{\delta T^0[\rho_N]}{\delta \rho_N(\mathbf{r})} - \frac{\delta T^0[\rho_{N-1}^\gamma]}{\delta \rho_{N-1}^\gamma(\mathbf{r})} \\ &= v_{hxc}^\gamma([\rho_{N-1}^\gamma]; \mathbf{r}) - v_{hxc}^\gamma([\rho_N]; \mathbf{r}) + \mu_N - \mu_{N-1}^\gamma. \end{aligned} \quad (30)$$

The dependence of $\rho_{N-1}^\gamma(\mathbf{r})$ on γ is through the γ dependence of the potential $v_{\text{ext}}^\gamma([\rho_N^\gamma]; \mathbf{r}) = v^\gamma(\mathbf{r})$. Using (30) in (28) and since

$$\frac{\partial}{\partial \gamma} (N-1) = \int d^3 r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} = 0, \quad (31)$$

it follows

$$\int d^3 r' \int d^3 r (v_{hxc}^\gamma([\rho_N]; \mathbf{r}) - v_{hxc}^\gamma([\rho_{N-1}^\gamma]; \mathbf{r})) \left. \frac{\delta \rho_{N-1}^\gamma(\mathbf{r})}{\delta v^\gamma(\mathbf{r}')} \right|_{N-1} \frac{\partial v^\gamma(\mathbf{r}')}{\partial \gamma} = 0. \quad (32)$$

The functional derivative with respect to v^γ is taken at constant particle number since ρ_{N-1}^γ and ρ_N are derived from the groundstates of the Hamiltonian in Eq. (8).

The author recently showed that [26]

$$\begin{aligned} & E_{hxc}^\gamma[\rho_N] - E_{hxc}^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3 r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \frac{\delta}{\delta \rho_N(\mathbf{r})} E_{hxc}^\gamma[\rho_N]. \end{aligned} \quad (33)$$

Take the functional derivative of (33) with respect to $v^\gamma(\mathbf{r})$ and use the functional chain rule:

$$\begin{aligned} & \int d^3 r' (v_{hxc}^\gamma([\rho_N]; \mathbf{r}) - v_{hxc}^\gamma([\rho_{N-1}^\gamma]; \mathbf{r})) \left. \frac{\delta \rho_{N-1}^\gamma(\mathbf{r}')}{\delta v^\gamma(\mathbf{r})} \right|_{N-1} \\ &= \int d^3 r'' \int d^3 r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \left. \frac{\delta v_{hxc}^\gamma[\rho_N; \mathbf{r}']}{\delta \rho_N(\mathbf{r}'')} \frac{\delta \rho_N(\mathbf{r}'')}{\delta v^\gamma(\mathbf{r})} \right|_N. \end{aligned} \quad (34)$$

Multiply both sides by $\frac{\partial v^\gamma(\mathbf{r}'')}{\partial \gamma}$ and integrate over \mathbf{r}'' . It follows from (34) and (37) that

$$\int d^3 r \int d^3 r' \int d^3 r'' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta v_{hxc}^\gamma[\rho_N; \mathbf{r}']}{\delta \rho_N(\mathbf{r})} \chi_N^\gamma(\mathbf{r}, \mathbf{r}'') \frac{\partial v^\gamma(\mathbf{r}'')}{\partial \gamma} = 0 \quad (35)$$

where

$$\chi_N^\gamma(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta \rho_N(\mathbf{r})}{\delta v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}')} \right|_N \quad (36)$$

is the density response function of the N -electron system. From stability considerations $\chi_N^\gamma(\mathbf{r}, \mathbf{r}')$ is negative semi-definite and has one zero eigenvalue which corresponds to the invariance of the density when the potential is changed by a constant [11, 12]. However, from (6)

$$\frac{\partial v^\gamma(\mathbf{r}'')}{\partial \gamma} = -v_{hx}([\rho_N]; \mathbf{r}) - \frac{\partial}{\partial \gamma} v_c^\gamma([\rho_N]; \mathbf{r}) \neq 0, \quad (37)$$

Hence, from the properties of $\chi_N^\gamma(\mathbf{r}, \mathbf{r}')$ Eq. (35) implies the main result of this paper,

$$\int d^3 r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta v_{hxc}^\gamma[\rho_N; \mathbf{r}']}{\delta \rho_N(\mathbf{r})} = \text{constant} \quad (38)$$

since $\frac{\delta v_{hxc}^\gamma[\rho_N; \mathbf{r}']}{\delta \rho_N(\mathbf{r})} = \frac{\delta E_{hxc}^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r}) \delta \rho_N(\mathbf{r})}$.

III. DISCUSSION AND SUMMARY

In the derivation of Eq. (38) use was made of the groundstate wavefunctions of the same Hamiltonian, for example in the derivation of (25). Accordingly the relation (38) has been proven for v -representable pure state densities [11, 12] only. Whether it is valid for non- v -representable densities and non-integer densities remains an open question which is under investigation. Throughout the assumption was made that all functional derivatives are well behaved and this implies that the functionals are defined for non-integer particle numbers as discussed in [11, 12, 23].

In summary, an integral expression was derived for the second derivative of the pure state density functional Hartree plus exchange-correlation energy which provides new insight into the structure of density functionals. It also places constraints on potential approximate exchange-correlation functionals and can be used to test existing and potential approximate functionals.

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